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ELECTROTRANSPORT OF CARBON,
NITROGEN AND OXYGEN IN ZIRCONIUM

M. S. Thesis Submitted to Iowa State University, February 1972

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Electrotransport of carbon,
nitrogen and oxygen in zirconium

by

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ABSTRACT

From electrotransport studies the mobilities, effective charges and diffusion coefficients of carbon, nitrogen and oxygen in β zirconium were determined at 1625, 1700 and 1800°C. In conjunction with this investigation the specific resistivity and solid solubility of carbon in β zirconium were also determined as a function of temperature. Efforts to purify zirconium by electrotransport were severely limited by the low mobility of carbon. Attempts to prepare zirconium metal with a low carbon content by the van Arkel process for use in subsequent electrotransport purification experiments are described.

INTRODUCTION

When a direct current is passed thru a pure metal or alloy in the solid or liquid state atomic components are transported relative to each other in addition to the normal movement of charge carriers (electrons and holes). This phenomenon is referred to herein as electrotransport but it is sometimes called electromigration or electrodiffusion. Electrotransport in solids has been the subject of much recent theoretical investigation. It has also been used for the preparation of ultra-pure metals (1), but as a commercial process for refinement of metals, the electrical energy requirements make the cost prohibitive for all but small quantities of special research materials. Electrotransport is also of practical concern in the field of solid state devices and microcircuits where conduction and shortcircuiting problems develop in wires and thin films due to the transport of the bulk material and void migration (2).

Investigations of electrotransport in solid metals have been conducted as early as 1930 but current interest has its beginning with the work of Seith and Wever (3) in the mid 1950's. General reviews have been given by Schwarz (4) and Heumann (5). Verhoeven (6) has published a comprehensive review of the state of the field up to 1963.

Jost (7) has described some of the essential features of electrotransport experiment in a simplified manner. When a small diameter rod is placed between two heavy electrodes as

in Figure 1a, resistance heating of the rod by a strong electric current causes a temperature distribution as shown in Figure 1b. Under a constant current the mid-section of the rod can be maintained at a uniformly high temperature sufficient for transport to become observable. According to Jost this temperature is not determined by heat conduction to the electrodes, but only by conduction thru the surrounding gases and eventually by convection and by radiation. A displacement of the components of the rod due to the electric field might now take place causing a decrease in the mass of the rod near one end along with a corresponding increase of mass at the other end. Figure 1c illustrates the phenomenon for transport of mass to the negative electrode.

Figure 1. From Jost (7) (a) Experimental Arrangement, (b) Temperature Distribution, (c) Mass Transfer toward the Negative Electrode in a Metal.

During electrotransport the atoms of a material are not neutral in an electric field and are polarized due to differences in ionizing behavior about which little is understood. Matrix atoms of a pure metal or solute atoms of an alloy may migrate either toward the anode or the cathode. This direction, to date, has only been determined experimentally since no theory adequately predicts in which direction an atomic component will move. Kuzmenko (8), in a study of self transport (i.e. transport of matrix atoms in a pure metal) of the metals Ag, Cu, Au, Al, Zn, Cd and Sn has shown these metals to be anode directed while Huntington (9) states that Co and Fe migrate toward the cathode. Warner (10) has tabulated the direction in which interstitial atoms move in various solid metals showing that with few exceptions these impurity atoms all tend to migrate in one direction within the same metal. Heumann (5) has compiled the work of several investigators showing the direction of transport for the substitutional atoms of a binary alloy.

The electrotransport process concentrates the impurities in the anode or cathode section of a rod, in opposition to the concentration-gradient diffusion which tends to cause complete dispersion. Field strength, current density, temperature and type of migrating component are important factors in determining the migration velocity.

ELECTROTRANSPORT MECHANISM OR THEORY

Until recently there has not been a great deal of agreement between different investigators as to the theoretical explanation for electrotransport phenomena. It is now widely accepted that the driving force responsible for mass transport in metals is due more directly to momentum exchange with the charge carriers than to the electrostatic field (9).

Under the influence of an electric field the atoms within a metal can assume either a positive or negative charge. These charged atoms or ions may be matrix metal atoms, substitutional atoms or interstitial atoms. Since this work deals with the interstitial atoms of carbon, nitrogen and oxygen, this treatment will be limited to the interstitial ions of these elements. The field force acting upon each ion within a metal is

$$F_i = eEZ_i$$

1

where e is the charge on the electron, E , the field strength and Z_i is a parameter which measures the direct interaction of the electrostatic field with the ion and is referred to as the true electric charge.

In most cases the dominating force on an ion subjected to an electric field is that due to the momentum exchange with the charge carriers. This force is often called the "electron drag"

force and an ion which is able to transfer momentum is referred to as an "activated ion". The frictional force between the ion and electron is written as

$$F_{ei} = -\delta_{ei}E \quad 2$$

where δ_{ei} is the "drag" or frictional coefficient and the negative sign is used because the force is in a direction opposite to the normal movement of an ion in an electric field. The frictional coefficient consists of a carrier concentration term, a scattering cross section value and a mean free path term for the charge carrier.

The total force acting upon an ion during electrotransport is the sum of the field force and frictional force or

$$F_T = F_i + F_{ei} = eE \left(Z_i - \frac{\delta_{ei}}{e} \right) \quad 3$$

In an ideal metal having a perfect crystalline array of identical atoms the total force would be zero and Z_i would equal $\frac{\delta_{ei}}{e}$. However in a real metal a condition of electroneutrality does not exist and Z_i never equals $\frac{\delta_{ei}}{e}$. Consequently, even in pure metals electrotransport will occur since normal lattice ions become activated and so experience a net electric force relative to the normal lattice.

Verhoeven (6) has presented a theoretical treatment of electrotransport in metals. Except for some variations the following treatment is from his review of the subject.

An activated ion in an alloy of uniform composition moves with a terminal velocity when subjected to an applied external field. The ion in passing thru the metal is hindered by collisions with the lattice atoms and the effect of these collisions determines the magnitude of the terminal velocity. The absolute mobility, B_i , is given as the terminal velocity, v_i , per unit of force or

$$B_i = v_i / F_T . \quad 4$$

From the theory of Brownian motion, Einstein has related the diffusion coefficient to the absolute mobility in terms of the Boltzmann constant and the absolute temperature such that

$$B_i = \frac{D_i}{kT} . \quad 5$$

The velocity of an ion in a crystalline solid under the influence of an electric field can be determined from Equations 3, 4 and 5 as

$$v_i = B_i F_T = \frac{D_i}{kT} eE \left(Z_i - \frac{\delta_{ei}}{e} \right) . \quad 6$$

The electric mobility, u_i , is defined as the velocity per unit electric field, v_i/E , and in terms of Equation 6 can be expressed as

$$u_i = \frac{D_i}{kT} e \left(Z_i - \frac{\delta_{ei}}{e} \right) . \quad 7$$

Neither the true charge, Z_i , on a component nor the frictional coefficient, δ_{ei} , can be determined directly from transport type experiments and therefore the terms in parenthesis are collectively referred to as the effective charge, Z^* , which is field independent. The mobility is now written as

$$u_i = \frac{D_i}{kT} eZ^* .$$

8

Since u_i and D_i are obtained experimentally from electro-transport data as seen later in this work, Z^* can be obtained from Equation 8. The sign of the effective charge indicates the direction in which an ion in a pure metal or an alloy can be expected to move. From Equation 3 it can be seen that when the field force is greater than the friction force Z^* is positive and transport proceeds to the cathode but since the frictional force generally predominates, in most cases Z^* will have a negative sign and transport occurs toward the anode.

EXPERIMENTAL METHOD

Apparatus

In order to obtain the electrotransport data the material under study was subjected to two conditions. First it had to be under the influence of an electric field to produce a directional transport of interstitial atoms and secondly the material had to be maintained in a low pressure system to avoid contamination. The electrotransport apparatus therefore consisted of two electrodes that support the rod specimen surrounded by a vacuum chamber. The chamber shown in Figure 2 was made of stainless steel with an inside diameter of $3 \frac{3}{4}$ inches and an inside length of 6 inches. A viewing port mounted on the chamber at an angle of 45° provided the means of measuring the temperature with an optical pyrometer.

The chamber was attached to the vacuum system by means of connecting flanges. An NRC Diffusion Pump model HS4-750 was used to obtain the desired low pressures. The chamber was "rough pumped" thru the diffusion pump using a Welch Duo Seal Mechanical Pump model 1397B. To prevent backstreaming of pump fluid molecules into the chamber an NRC Optical Baffle Cold Trap model HB4 was mounted vertically between the diffusion pump and the vacuum chamber. The internal reservoir/baffle was cooled by mechanical refrigeration using Freon as a coolant.

Figure 2. Schematic of the Experimental Apparatus Used in the Study of Electrotransport.

The electrodes of 3/4 inch diameter stainless steel were set horizontally into the chamber and were insulated from the chamber by bakelite and teflon spacers. Rubber O-rings provided a vacuum seal. Tantalum "U" shaped adapters converted the heavy electrodes to a size which would fit the dimensions of the material under study as show in Figure 3. By varying the size of the "U" shaped adapters the thermal gradient across the length of the sample could be minimized and the effect of thermodiffusion reduced. The "U" shape allowed for the thermal expansion taking place with increased temperature upon internal resistance heating of the sample. Copper cooling coils were soldered around the outside of the heavy electrodes, chamber and sight glass tube.

Material

The zirconium used in this study was prepared by the iodide-decomposition process (11). The original crystal bar material was 1/2 inch in diameter and was arc melted in a purified inert gas atmosphere into a small rod-shaped ingot called a "finger". After chemical cleaning in a solution of 45 parts HNO_3 + 45 parts H_2O + 10 parts HF (12) the finger was sectioned for analyses. Metallic impurities were determined by spectrographic analysis (13, 14). Vacuum fusion analysis in a liquid platinum bath was used to determine the oxygen and nitrogen content (15). The carbon contents of the starting

Figure 3. Zirconium Sample with Supporting Tantalum Adapters and Electrodes
[From Peterson et al.(16)].

material were determined by chromatographic analysis of CO_2 after combustion in oxygen. Table I gives the results of the analysis of the base material. The major portion of the finger was swaged into a rod of 0.260 cm diameter and was used for the low carbon, oxygen and nitrogen sections of an electrotransport rod.

The high interstitial alloys were prepared by adding the desired solute to the base material. For the high oxygen material, a calculated amount of ZrO_2 powder was added to a cavity bored into the finger of the low concentration material and sealed in with a zirconium plug. The finger was then carefully arc-melted a total of 9 times to insure homogeneity within the sample. The high nitrogen alloy was prepared by arc melting the zirconium under a predetermined partial pressure of nitrogen gas. Zirconium being a good gettering material readily absorbed the nitrogen during repeated melting of the finger to insure a homogeneous sample. The high carbon alloy was prepared in a manner similar to that of the high oxygen alloy. Carbon was added as amorphous carbon which contained 8 millicuries of ^{14}C per gram.

Each finger was chemically cleaned, sampled, and submitted for analysis by the methods mentioned earlier. The fingers were then swaged into rods of 0.260 cm diameter. The analyses of the high concentration alloys are shown in Table II.

Table I. Analysis of Iodide-Refined Zirconium

<u>Impurity</u>	<u>Analysis, ppm</u>
Al	d<30
C	25
Ca	d<20
Co	-
Cr	-<40
Cu	d<30
Fe	d<50
H	5
Hf	600
Mg	-<20
Mn	-
Mo	-
N	4
O	125
Si	~100
Ta	-

Symbol Meaning

- Not detected
 -< Not detected, less than
 d< Detected, less than
 ~ Approximately

Table II. Analysis of High Concentration Alloys

<u>Alloy</u>	<u>Analysis, ppm</u>
High Carbon	510
High Oxygen	750
High Nitrogen	400

Procedure

Rods of 6.6 cm length were found to be long enough to satisfy the condition of infinite length. These rods consisted of a 2.2 cm length segment of the base material and a 4.4 cm segment of the high concentration material. Each section was threaded on one end and then electropolished in a solution of 6% perchloric acid and 94% methyl alcohol at a dry ice-acetone temperature of approximately -76°C (17). The polished section were then butt welded together in a vacuum chamber. The welds were inspected for soundness and consistency of rod diameter, the lack of which would affect the assumption of constant current density. Should a weld have some small undetected unsoundness, its defective condition should improve with time since the movement of atoms at the temperature of these experiments should soon fill any voids at the weld interface.

After each run the vacuum chamber was thoroughly cleaned with acetone and methyl alcohol. The butt-welded rod was then threaded into the tantalum adapters and fitted into the electrodes in the vacuum chamber. Since it was known that oxygen moves toward the anode under the influence of a direct current (18), the low concentration end of the rod was connected to the cathode so that electrotransport would oppose the chemical diffusion due to the concentration gradient. Nitrogen and carbon were also found experimentally to be anode seeking atoms.

The system was "rough pumped" while hot water circulated thru the copper coils on the outside of the chamber to facilitate outgassing. After 16 hours a pressure of about 5 microns was obtained and the diffusion pump was started. When a pressure of 9×10^{-7} torr was obtained the sample was heated and cold water was circulated throughout the coils to prevent continued outgassing of the chamber and to protect the teflon and rubber seals.

The amount of current that can be passed thru a rod must be balanced by the amount of thermal energy that is removed, otherwise the temperature of the rod will increase and eventually melt. Some investigators have used small diameter wires and thin strips with high surface to volume ratios to increase the amount of heat loss to the surroundings and thus to attain a higher current density. However the total mass of the material in these strips and wires is quite limited and hence only a small number of samples per length can be obtained. Furthermore, the advantageous effect of increasing the ratio of the surface area to the cross-sectional area in order to achieve a larger electric field and hence a higher impurity velocity, is counterbalanced by the effect of the larger relative surface area increasing the rate of possible contamination by the environment within the chamber.

The sample was heated to the desired temperature by its internal resistance. A direct current was provided by a saturable core step down transformer which provided a full-wave-rectified current with a 15% ripple. The current densities required for the experimental temperatures of 1625° to 1800°C ranged from 1325 to 1800 amps per sq. cm of zirconium sample rod.

The true temperature of the rod was determined by preparing a calibration curve of apparent surface temperature vs black body temperature. This was done by drilling a series of small holes along the axis of the rod. The black body temperature of each hole and the adjacent surface temperature were measured with an optical pyrometer. The measurements were corrected for the absorption of radiation by the sight glass and the thin film of zirconium, if any, deposited upon it. From this calibration curve the true temperature of any specimen could be determined from its observed surface temperature. The systematic error involved in the temperature measurement is $\pm 10^{\circ}\text{C}$ at a temperature of 1800°C.

Although the tantulum adapters helped to obtain a constant temperature across the length of the sample, in actuality a difference of about 25°C existed between the center and the ends of the rod. The region just to the right of the weld interface

was held at 1625°, 1700° and 1800°C, the temperatures selected for these experiments. Since this region was used to determine the displacement of the interstitial atom due to electrotransport it was also used for the temperature reference.

During an actual electrotransport run, the temperature was raised by slowly increasing the current from the transformer so as to reduce any distortion which might occur in the rod due to the phase transformation. When the operating temperature was reached it was maintained by intermittently checking the surface temperature with an optical pyrometer. A pressure of less than 10^{-6} torr was maintained in the system during these experiments. At the conclusion of the transport experiment the power was turned off and the sample was allowed to cool quickly to room temperature.

Determination of Concentration Profile

Oils or dirt films would cause errors in analyses of the rod; therefore, nylon gloves were used to handle the specimens at all times. The rod was cut into segments of about 0.3 cm by use of clean diagonal cutters. Each segment was labeled in consecutive order along the length of the rod. The segments of the rods containing nitrogen or oxygen were then analyzed by the Ames Laboratory Analytical Service Group using the methods mentioned earlier. The precision of the analytical determinations were found to be $\pm 3\%$. The exact length of

each segment was determined from the specimen weight assuming constant density and cross-sectional area of the rod. Mid-points of the consecutive segments were then correlated to their interstitial concentration and a concentration vs distance profile was drawn.

Since carbon analysis by the combustion method yielded scattered results in previous electrotransport studies (19), radioactive ^{14}C was used as a tracer element to follow the carbon migration. A profile of distance along the rod vs radioactivity in counts per minute was plotted corresponding to the concentration profiles of oxygen and nitrogen. The procedure was to cut the 6.6 cm rod into 20 equal segments using a thin carbide cutting wheel. Each segment was mounted in the exact center of a mold and self-curing acrylic resin was poured around it and allowed to solidify forming a disc. The disc was ground thru 600 grit paper until both ends of the specimen were exposed and flat. The thickness of the segment was then measured with a micrometer. The discs were placed in a Sharp LB-100 Series Lowbeta gas-proportional-measuring system. The β activity of each end of the specimen was measured for 10 minutes and the two counts were averaged. The background activity was subtracted from this value and the difference was used as the level of the activity for the midpoint of the segment. The results from this method were also found to have a precision of $\pm 3\%$.

SUPPORTING EXPERIMENTAL DETERMINATION

Carbon Solubility

That the kinetics of a diffusion process can be significantly affected by a small degree of supersaturation has been discussed by Guy (20) in his study of vacancies during electrodiffusion. Peterson et al. (16) have pointed out that the diffusion coefficient cannot be determined when the solubility limit of the interstitial atom in the electrotransport rod is exceeded. The phase diagrams indicate that the solubility of oxygen in zirconium (21) at temperatures above 1600°C is greater than 8 a/o or 15,000 ppm and the solubility of nitrogen (22) above 1600°C is greater than 3 a/o or 4700 ppm. Inasmuch as the initial concentrations of the high oxygen and high nitrogen alloys were well below the solubility limits no precipitation of oxides or nitrides at the anode end were encountered.

The study of carbon transport was hampered by the lack of data on the solubility of carbon in β zirconium. The only information found in the literature was some limited metallographic work by Samsonov and Rozenova (23) who estimated the carbon solubility to be less than 6400 ppm. It was therefore necessary to determine the solubility of carbon in β zirconium in the temperature range of interest to make sure that solubility limit was not exceeded in any of the electrotransport studies.

Zirconium alloys containing 450, 700, 1100, 2700 and 7500 ppm carbon were prepared by arc melting. These were swaged and then machined to give a tapered rod 3 inches long with the diameter of the small end 0.100 inches and the large end 0.192 inches. Temperatures were measured adjacent to small fiducial marks made at 1 cm intervals along the length of the rod. The vacuum chamber described previously was modified to provide a means for water quenching a sample rod. The rod was heated by the passage of an alternating current thru the specimen thus eliminating any possible electrotransport effects. These tapered rods were quickly brought to a temperature range which included the interval between 1200° and 1800°C. The rods were held at this temperature for one hour. This was long enough to achieve equilibrium but a short enough period to minimize the amount of thermodiffusion. The rods were then quenched by flooding the chamber with water. Upon microscopic examination, all of the rods except the one containing 7500 ppm C exhibited a distinct interface somewhere along the rod corresponding to the boundary separating the homogeneous and heterogeneous phase fields.

Knowing the temperature profile along the length of the rod, the temperature at the interface was determined. This corresponded to a point on the solvus. An Arrhenius plot of the carbon solubility in the range from 1175°C to 1800°C

is shown in Figure 4. The log solubility vs reciprocal temperature plot shows a good straight line fit for the data. The straight line can be expressed in the form

$C = C_0 \exp(-\Delta H/RT)$ with C , the concentration in atom percent, and ΔH , the heat of solution of ZrC in β zirconium in calories per mole. The carbon solubility at a temperature between 1175° and $1800^\circ C$ is given as

$$C = 160 \exp\left(\frac{-17,400}{RT}\right)$$

9

Specific Resistance

Before the mobilities of the interstitial solutes in β zirconium could be calculated the specific resistivity over the temperature range of 1600° to $1800^\circ C$ had to be known. Gebhardt et al. (24) determined the resistivity of recrystallized iodide zirconium containing 69 ppm hafnium up to $1780^\circ C$. Cook et al. (25) reported resistivity vs temperature profiles for crystal bar zirconium containing 1.8 w/o hafnium. Neither Gebhardt nor Cook reported the oxygen content of their material. Since the resistivity of zirconium is known to be dependent upon the oxygen content, the specific resistivity of the material used in this investigation was measured as a function of temperature.

Following the method described by Chiotti (26), the rod of 9.9 cm length with a uniform cross section of 0.056 cm^2 was placed between two heavy water-cooled copper electrodes

Figure 4. Arrhenius Plot of Solubility of Carbon in β Zirconium.

and enclosed in a vacuum tight chamber containing a sight glass port. The rod contained a black body hole for temperature measurement centered between two small zirconium electrical contact wires used for measurement of the resistance. The small contact wires 0.013 cm in diameter and 1.038 cm apart were spot welded to the rod in a vacuum using the Hughes miniature welder described previously. The rod was heated by passage of a 60 cycle alternating current thru it. The resistance of the specimen was measured potentiometrically from the recorded voltage drop and the dimensions of the specimen. A straight line was obtained from the plot of specific resistivity vs temperature between 1000°C and 1675 C as shown in Figure 5. A linear extrapolation to the melting point is shown. The results of these measurements are in fair agreement with the data given by Gebhardt.

Figure 5. Specific Resistivity of β Zirconium as a Function of Temperature.

PRESENTATION AND ANALYSIS OF ELECTROTRANSPORT DATA

The concentration vs distance curves for nitrogen, oxygen and carbon at temperatures of 1625°, 1700° and 1800°C are shown in Figures 6 thru 8. In the nitrogen and oxygen profiles, the concentration is plotted in parts per million while in the carbon profiles, the concentration is plotted as a function of the ^{14}C beta activity in counts per minute.

Before the electrotransport run a large concentration difference existed at the weld interface at a distance, d , of 2.2 cm from the cathode end of the rod. In a pure diffusion experiment the diffusion curve would pivot around the point on the weld interface at the median concentration of the two sections. However in electrotransport an additional movement of atoms takes place due to the impressed electric field. It is this effect which causes a displacement, ΔX , of the concentration profile away from the weld interface. Such is the case shown in Figure 6. From this displacement, ΔX , and the time, t , the mobility of an interstitial atom, u_i , can be obtained by the equation

$$u_i = \frac{\Delta X}{Et} \quad . \quad 10$$

The electric field, E , was calculated from the current density required to maintain the rod at the experimental temperature and the resistivity of the zirconium at that temperature taken from the graph in Figure 5.

NITROGEN CONCENTRATION PROFILES

CES 1-131 1625°C FOR 14 HRS FIGURE 6a

CES 2-13 1700°C FOR 10 HRS FIGURE 6b

CES 2-1 1800°C FOR 8 HRS FIGURE 6c

Figure 6. Nitrogen Concentration Profiles.

OXYGEN CONCENTRATION PROFILES

CES I-79 1625° FOR 7 HRS FIGURE 7a

CES I-81 1700° FOR 4 HRS FIGURE 7b

CES I-62 1800° FOR 2 HRS FIGURE 7c

Figure 7. Oxygen Concentration Profiles.

^{14}C ACTIVITY PROFILES

CES 2-5 1625°C FOR 50 HRS. FIGURE 8a

CES 1-97 1700°C FOR 27 HRS. FIGURE 8b

CES 1-93 1800°C FOR 24 HRS. FIGURE 8c

Figure 8. ^{14}C Activity Profiles.

As shown by Peterson et al. (16) the mass transport of an interstitial atom in a rod of semi-infinite length under the influence of a direct current is described by

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial X^2} + u_i E \frac{\partial C_i}{\partial X} \quad 11$$

where C_i is the interstitial concentration at any point along the length of the rod, and D_i is the diffusion coefficient for the interstitial atom. The differential equation is only valid if it is assumed that u_i , D_i and E are independent of concentration and for this study the assumption is possible because of the low levels of interstitial concentration.

If at the weld interface where $d = 2.2$ cm the value of X is set equal to zero, the initial conditions are given as:

$$C_i = C_L \text{ at } X < 0 \text{ and } t = 0$$

$$C_i = C_H \text{ at } X > 0 \text{ and } t = 0$$

12

The direct current thru the specimen was terminated before the high concentration plateau disappeared into the concentration increase at the anode end of the specimen and hence the boundary conditions can be written as:

$$C_i = C_L \text{ at } x = -\infty \text{ and } t = t$$

$$C_i = C_H \text{ at } X = +\infty \text{ and } t = t$$

13

Fick's second law for unidirectional flow in the absence of an electric field is

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial X} \left(D_i(C_i, X, T) \frac{\partial C_i}{\partial X} \right) \quad 14$$

showing the diffusion coefficient D_i as a function of concentration, distance and temperature. Equation 14 reduces to

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial X^2} \quad 15$$

when D_i is independent of concentration and distance. The solution to Equation 15, subject to the initial conditions 12 involves an error function (27) and is given by

$$C_i = C_L + \frac{C_H - C_L}{2} \left(1 + \operatorname{erf} \frac{X}{2\sqrt{D_i t}} \right) \quad 16$$

This treatment was used by Grube and Jedele (28) to determine diffusion coefficients.

The Grube method can be used to determine the diffusion coefficients during an electrotransport experiment. The solution to Equation 11 under the initial and boundary conditions 12 and 13 gives the following equation (16):

$$C_i = C_L + \frac{C_H - C_L}{2} \left[\operatorname{erfc} - \left(\frac{X \pm u_i E t}{2\sqrt{D_i t}} \right) \right] \quad 17$$

where

$$\operatorname{erfc}(z) = 1 - \operatorname{erf} z \quad a$$

$$\operatorname{erf}(-z) = -\operatorname{erf}(z) \quad b$$

$$\operatorname{erf}(0) = 0 \quad c$$

$$\operatorname{erf}(\infty) = 1 \quad d$$

By rearranging 17 using the relation 17a the following equation is obtained

$$\frac{C_i - C_L}{C_H - C_L} = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{X + u_i Et_i}{2\sqrt{D_i t}} \right) \right] \quad 18$$

Since interstitial atoms move toward the cathode in zirconium, the value of $u_i Et$ or ΔX is positive. By letting $X' = X + u_i Et$ an equation similar to that of 16 is obtained

$$\frac{C_i - C_L}{C_H - C_L} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{X'}{2\sqrt{D_i t}} \right) \right] \quad 19$$

and the Grube Method can be applied. A plot of $\frac{C_i - C_L}{C_H - C_L}$ vs X

on probability paper will give a straight line as seen in Figure 9 obtained from the concentration profile of the nitrogen interstitial at 1625°C. Hall (29) has shown that the equation of a straight line on a similar probability plot is of the type

$$C/C_0 = \operatorname{erfc} (h\lambda + k) = \operatorname{erfc} u \quad 20$$

where C/C_0 is the ordinate, λ is the abscissa and h and k are the slope and intercept respectively and

$$\operatorname{erfc} u = \frac{1}{2} (1 + \operatorname{erf} u) \quad 21$$

In the probability plot of Figure 9 the $\frac{C_i - C_L}{C_H - C_L}$ ratio may be

Figure 9. Probability Plot of $\frac{C_i - C_L}{C_H - C_L}$ vs X .

equated to C/C_0 of Equation 20, and λ equated to X . Let a new abscissa be defined as $X' = X + u_1 Et$ then the straight line on Figure 10 would have the equation

$$\frac{C_i - C_L}{C_H - C_L} = \text{erfc} (mX' + k) = \text{erfc } z \quad 22$$

where X' is now the abscissa; the slope, m , is equal to $\frac{1}{2\sqrt{D_1 t}}$; k , the intercept, is now equal to zero and from Equation 21

$$\text{erfc } z = \frac{1}{2} (1 + \text{erf } z) \quad 23$$

The $\text{erf } z$ can now be found in terms of the concentration ratio or

$$\text{erf } z = 2 \left(\frac{C_i - C_L}{C_H - C_L} \right) - 1 \quad 24$$

If the right hand side of Equation 19 is substituted into Equation 24 it can be seen that

$$\text{erf } z = \text{erf} \left(\frac{X'}{2\sqrt{D_1 t}} \right) \quad 25$$

and thus

$$z = \frac{X'}{2\sqrt{D_1 t}} \quad 26$$

The value of z is obtained from Equation 24 using the table of error functions (30). It can be seen that $\text{erf } z$ equals 0 when the value of $\frac{C_i - C_L}{C_H - C_L}$ is 0.5. Since $z = 0$ when $\text{erf } z = 0$, X'

must also be zero when $\frac{C_i - C_L}{C_H - C_L}$ is 0.5. This therefore defines

the origin of the new coordinate system having an ordinate of z and an abscissa of X' shown in Figure 10.

Figure 10. z vs X' Superimposed on the Probability
Plot of $\frac{C_i - C_L}{C_H - C_L}$ vs X in Figure 9.

The diffusion coefficients were determined from Equation 26 by calculating D_i at three arbitrarily chosen points on the straight line using the time of electrotransport in seconds. The average of these was taken as the value of the diffusion coefficient at the temperature of interest. (Note: The diffusion coefficient may also be determined from the slope of the graph of z vs X' .)

The effective charge, Z^* was calculated from the mobility and the diffusion coefficient by the equation

$$Z^* = \frac{u_i kT}{eD_i} \quad 27$$

where k is Boltzmann's constant, e is the charge on the electron in coulombs and T is the absolute temperature at which the electrotransport experiment was made. The mobilities, diffusion coefficients and effective charges determined from the displacement, time and electric field during electrotransport at temperatures of 1625°, 1700° and 1800°C for nitrogen, oxygen and carbon interstitials in zirconium are given in Table III.

The combination of errors in t , ΔX and E give the value of the mobility, u_i , an error of approximately $\pm 20\%$. The random error in time is almost insignificant especially for transport over long periods. The error in ΔX is the most significant since it involves the error in chemical analysis

for obtaining the concentration profiles as well as the error in measurement of ΔX from the curve. The systematic error in E is derived from the error in the amperage plus the error in the specific resistivity.

Table III. The Electrotransport Velocities, Diffusion Coefficients, and Electric Charge, Z^* , for Carbon, Nitrogen and Oxygen in Zirconium.

Interstitial Solute	Temp, °C	ΔX cm	t, hr	E, V/cm	u_i $10^{-5} \text{ cm}^2/\text{V-sec}$	D_i $10^{-5} \text{ cm}^2/\text{sec}$	Z^*
Nitrogen	1625	0.32	14	0.189	3.4	0.33	-1.7
	1700	0.30	10	0.206	4.0	0.54	-1.3
	1800	0.38	8	0.237	5.6	1.2	-0.9
Oxygen	1625	0.55	7	0.168	13	1.4	-1.6
	1700	0.46	4	0.185	18	3.0	-1.0
	1800	0.60	2	0.204	41	3.8	-1.9
Carbon	1625	0	50	0.185	<0.50	0.39	-<0.2
	1700	<0.10	27	0.209	<0.50	0.50	-0.2
	1800	<0.10	24	0.230	<0.50	0.87	-0.1

The diffusion coefficient is probably accurate to $\pm 20\%$ mainly due to the limited number of sample sections along the length of the rod as well as the random errors in the chemical analysis itself. Another source of error in D_i is the possible variation in the slope of the probability plot of $\frac{C_i - C_L}{C_H - C_L}$ vs X .

Previously it had been mentioned that an error in temperature of $\pm 10^\circ$ at temperature of 1800°C could be expected which in percentage would be less than $\pm 1\%$. The error in Z^* , from Equation 27, can thus be seen to be almost entirely due to the combination of the errors in u_i and D_i . Therefore a reasonable estimate of the error in Z^* would probably be $\pm 40\%$.

The values for the diffusion coefficient are in good agreement with other research done on zirconium. Mallett et al. (22) determined the diffusion coefficient of nitrogen in β zirconium at 1600°C to be $0.27 \times 10^{-5}\text{cm}^2/\text{sec}$. A diffusion coefficient for oxygen in high purity zirconium could not be found in the literature but Mallett et al. (31) have determined the diffusion rates of oxygen in beta Zircaloy 2 in the range $1000^\circ - 1500^\circ\text{C}$. For beta Zircaloy 2 the variation of the diffusion coefficient, D , in cm^2/sec with temperature is given by the equation

$$D = 0.0453 \exp (-28,200/RT) . \quad 28$$

From Equation 28 an extrapolation to a temperature of 1625°C would yield a diffusion coefficient of $2.5 \times 10^{-5}\text{cm}^2/\text{sec}$. Using a tracer technique Andrievskii et al. (32) investigated the diffusion of ^{14}C in iodide zirconium and obtained a value of $0.33 \times 10^{-5}\text{cm}^2/\text{sec}$ at 1600°C .

PREPARATION OF HIGH PURITY ZIRCONIUM

Steady State Electrotransport Experiment

Just as the technique of zone melting had been known for many years before it found usefulness in the refinement of metals, the phenomenon of electrotransport has taken many years to be adapted to the purification of metals. Verhoeven (33) has shown that thru the use of electrotransport very large reductions in the concentrations of interstitial impurities should be possible and that the phenomenon could be used to produce small quantities of ultra-high-purity metals. Peterson (34) has described the experimental factors involved in applying electrotransport to metal purification. Using this technique, Carlson et al. (35) prepared vanadium metal having a resistance ratio ($R_{300^{\circ}\text{K}}/R_{4.2^{\circ}\text{K}}$) as high as 2850.

In order to evaluate the applicability of electrotransport to the purification of zirconium an experiment was conducted in an attempt to obtain some high purity material. In this experiment, a direct current was passed thru a zirconium rod for a time sufficient to obtain a steady state. At the steady state the transport of impurities due to the electric field is balanced by the diffusion of impurities in the opposite direction due to the chemical potential associated with the concentration gradient. Although the velocity of the solute is important during purification, the chief consideration is the concentration change which the field is capable of producing.

It has previously been stated that the interstitial impurities of carbon, nitrogen and oxygen move to the anode during electrotransport. The experiment was therefore arranged such that the cathode end of the rod would be purified. Purification of the cathode end continues until a steady state is reached. By comparing the resistance ratio of the cathode half of the rod after electrotransport to the resistance ratio of the original material, an evaluation of the success of the experiment could be determined. Although the resistance ratio cannot identify the impurities present it does reflect the total amount of solutes present.

A zirconium rod of 16.5 cm length and 0.260 cm diameter was fabricated from crystal bar material having the impurity content shown in Table IV and a resistance ratio of $64 \pm 10\%$. The rod of uniform composition was placed in the electrotransport apparatus which consisted of an all metal chamber having an electrode assembly similar to that shown previously in Figure 3 except that no rubber or teflon parts were used. Since the system was all metal it was possible to outgas the chamber at a temperature of 400°C . An Ultek ionization pump, model P-290, was used in combination with a titanium sublimation booster pump to obtain an initial pressure of 3×10^{-9} torr which decreased to 2×10^{-10} torr. The rod was maintained at a temperature of 1625°C for 102 hours using a current density of 1630 amps/cm^2 .

Table IV. Analysis of Crystal Bar Zirconium Used for
Steady State Electrotransport

<u>Impurity</u>	<u>Analysis, ppm</u>
Al	d<20
C	19
Ca	-<10
Co	-
Cr	d<20
Cu	~15
Fe	~30
H	5
Hf	-<300
Mg	-<5
Mn	-
Mo	-
N	23
O	25
Si	~30
Ta	-
Ti	<25

Symbol Meaning

- Not detected
 - < Not detected, less than
 - d< Detected, less than
 - ~ Approximately
-

The temperature and time interval were of primary importance. The rate of vaporization of zirconium at high temperatures and low pressures limited the temperature to 1625°C for extended periods of time. The time length for electrotransport was determined from the work done by Schmidt et al. (36). They showed that under similar electrotransport conditions a rod of 250 ppm nitrogen and 230 ppm oxygen attained a steady state condition within 5 days. Since maximum purification is obtained at the steady state a time interval of nearly 5 days was chosen.

Upon completion of electrotransport the rod was cut into four sections of equal length. The resistance ratio was measured on both halves of each section and these values are tabulated in Table V. The ratios in the cathode half of the rod were far below those expected since values of 1340 for zone-refined zirconium have been reported (37) after 20 passes.

Table V. Resistance Ratios along the Length of an Electrotransport Rod Maintained at 1625°C for 101 Hours and 45 Minutes.

Cathode Half				Anode Half			
1st Section		2nd Section		3rd Section		4th Section	
1st Half	2nd Half	1st Half	2nd Half	1st Half	2nd Half	1st Half	2nd Half
78.4	100	112	98.8	93.4	83.7	83.7	58.4

Because carbon has an extremely low mobility (see Table III) in zirconium, it would take electrotransport periods on the order of months for its movement from the cathode end. It was believed that the low resistance ratios in the cathode half of the rod were due, at least in part, to the presence of carbon. Easton and Betterton (37) after studies on the ultra-high vacuum zone purification of zirconium, have presented the following results.

Table VI. Effects of Impurities on the Resistivity and Resistance Ratios of Zirconium

Condition of Zirconium	Impurity Concentration Solute Conc.		Impurity Contribution to 4.2°K Resistivity	Resistance Ratio
As-received	O	22 wt ppm.	0.082 μ ohm-cm	90
Iodide-Zr	N	4.5	0.020	
	C	12	0.066	
Total Impurities		0.38 at.%	0.496	
Zone-purified	O	11 wt ppm.	0.042	450
6 Passes	N	0.5	0.002	
	C	8	0.044	
Total Impurities		0.02 at.%	0.095	
Zone-purified	O	4 wt ppm.	0.015	1340
20 Passes	N	-	-	
	C	1	0.004	
Total Impurities		0.005 at.%	0.031	

The above data indicate that the resistance ratio of zirconium is highly sensitive to interstitial impurities and a difference of 15 to 20 ppm in the total interstitial content can change the resistance ratio by as much as 1000. Note especially that the carbon contribution to the 4.2°K resistivity drops from 0.066 μ ohm-cm to 0.004 μ ohm-cm, a factor of 16, as the carbon content is reduced from 12 ppm to 1 ppm.

Peterson et al. (38) have reported a similar effect of carbon on the resistance ratio of thorium in which the 4.2°K of thorium changes by 0.0055 μ ohm-cm per one ppm carbon by weight. Inasmuch as the purest zirconium available for the transport purification experiment contains 10-20 ppm carbon, a small quantity of zirconium of very low carbon content was considered essential for this investigation.

Refinement by Iodide Decomposition

The removal of impurities from a metal becomes increasingly difficult as the impurity content within the metal decreases. To obtain the low carbon material needed for electrotransport, electron beam-melted reactor grade zirconium with the impurity content shown in Table VII was to be further refined by the iodide-decomposition or van Arkel process (39). The process is based on the fact that certain metallic iodides are decomposed by contact with a hot filament so that the metal is deposited on the

Table VII. Analysis of Electron Beam-Melted Reactor Grade Zirconium

<u>Impurity</u>	<u>Analysis, ppm</u>
Al	d-<30
C	13
Ca	~10
Co	-
Cr	~75
Cu	<5
Fe	d<150
H	4
Hf	-<100
Mg	~5
Mn	-<50
Mo	-<50
N	3
O	103
Si	-<50
Ta	-
Ti	<20

Symbol Meaning

- Not detected
 - < Not detected, less than
 - d< Detected, less than
 - ~ Approximately
-

filament. In the case of zirconium, the iodine serves as a vehicle which combines with the crude metal at a temperature of 250°C , forming the tetraiodide. The temperature of the process is so controlled that the tetraiodide is vaporized and pure metal is deposited on the zirconium filament heated to a temperature of 1300°C . Since zirconium has such a strong affinity for hydrogen, oxygen, nitrogen and carbon, the process is necessarily one involving a high vacuum. Elaborate precautions were taken to eliminate all possible sources of carbon contamination within the system. The feed material can be purified with respect to carbon and most other contaminants with the exception of those elements that also form readily decomposable iodides such as hafnium and titanium. Bulkowski et al. (40) has shown that the transfer ratio of carbon from the feed to the filament is 0.02-0.11 for crude zirconium containing 2900 ppm carbon.

A glass system was designed to obtain material of low carbon content since contamination from the glass would be minimal. The system consisted of a vycor reaction vessel which contained the feed zirconium, a vessel head thru which two tungsten electrodes were mounted by glass-to-metal seals and a separate pyrex iodine container. Many difficulties were experienced with a glass system. The apparatus required a great deal of time and skill from an experienced glassblower and even then the apparatus was

fragile. The glass system was abandoned after considerable time and a number of unsuccessful attempts due to sealing problems and attack of the filament by the iodine vapor.

An all metal system for the iodide-decomposition process was then designed and constructed as shown in Figure 11. It consisted of a reaction vessel, vessel head and capsule breaker assembly constructed of niconel because of its excellent iodine corrosion resistance, low carbon content and relatively good machining and welding properties. The vessel head contained a vacuum duct, a viewing port and a copper feedthrough assembly. Tungsten electrodes were threaded into the copper feedthroughs which were protected by glass tubing. The zirconium filament was wound around the tungsten electrode tips and extended a length of 4 inches into the reaction vessel which contained the turnings of crude zirconium held in place by a molybdenum retaining screen. High vacuum seals were provided by "Curvac" flanges and OFHC copper gaskets.

The reaction vessel was connected to a high vacuum system similar to that described on page 39 by the use of a valve containing a "Viton" elastomer O-ring. Except for this valve the entire vacuum system and niconel reaction vessel were bakeable to 400°C for outgassing purposes. A pressure of 3×10^{-9} torr was attained before closing the valve and subsequent removal of the vessel from the vacuum system.

Figure 11. Inconel Reaction Vessel for Refinement of Zirconium.

The evacuated Inconel vessel was wrapped with heating tapes and raised to a temperature of 250°C. The filament was then heated to a temperature of 1300°C by an alternating current transformer using an optical pyrometer to determine the temperature. Using the breaker assembly, the capsule containing 20 grams of crystalline iodide was fractured. The iodide immediately sublimed and completely engulfed the system. Due to the corrosive nature of iodine, the filament of only 0.031 inch diameter zirconium wire quickly failed.

A study into the thermodynamics of the reaction:

provides an explanation for the corrosion of the filament at 1300°C. Sale (41) has shown that the decomposition temperature of zirconium tetraiodide, ZrI_4 , is a function of the pressure within the system. From his discussion, it can be seen that if the iodine within the system were to momentarily reach a pressure of 10^{-2} atmospheres, the decomposition temperature of the ZrI_4 would be 1500°C. By the ideal gas law, the attainment of a pressure of 10^{-2} atmospheres at a temperature of 250°C would require only 0.01 grams of iodine for the volume within the reaction vessel. Since the temperature of the filament was not above the ZrI_4 decomposition temperature for the iodine pressure

attained within the system at the instant the bulb was fractured, a highly corrosive atmosphere of iodine vapor existed.

From this experience and those involving the glass system, it was realized that the use of ZrI_4 as the iodine source should eliminate the problem of filament corrosion. Zirconium tetraiodide was made by mixing stoichiometric amounts of zirconium and iodine in a quartz tube contained in a stainless steel reaction vessel. The stainless steel vessel was then heated slowly to a temperature of 500°C and allowed to cool slowly. Since ZrI_4 is very hygroscopic and decomposes readily in moist air the product of the reaction was removed from the reaction vessel in an evacuated glove box. The ZrI_4 was purified by distillation under a dynamic vacuum and then sealed in a small glass capsule.

Except for the use of a capsule containing ZrI_4 the same procedure mentioned above was followed and zirconium was successfully grown on the filament. A crystal bar filament of 0.080 inch diameter was produced before the reaction stopped due primarily to the condensation of the iodide near the valve containing the "Viton" O-ring. Condensation occurred near the O-ring since its upper temperature limit was 175°C while the rest of the vessel was at a temperature of 250°C .

After removal from the apparatus, the U-shaped filament was bent into a straight rod. The force required to bend

the filament led to some concern as to the purity of the deposited zirconium, since crystal bar or iodide-refined zirconium is normally very soft and ductile. The fear of contamination was verified when chemical analysis of the filament revealed that the carbon content increased from 12 ppm in the original filament to 380 ppm in the as-grown crystal bar.

In spite of the extreme care taken to eliminate carbon from the system, the above results indicated that a rather large source of carbon contamination existed. One possible source was the ZrI_4 since its purification involved only one sublimation. Highly purified ZrI_4 obtained from Dr. E. M. Larsen of the Chemistry Department, University of Wisconsin, was sealed into a small glass capsule for use in the next experiment. The other and more likely source was believed to be the "Viton" O-ring within the vacuum valve. An Ultek Quad 150 Residual Gas Analyzer connected into the ultra-high vacuum system was used to monitor the constituents contributing to the pressure change of the dynamic vacuum system. An amplified signal from the ion detector of the analyzer was transmitted to an oscilloscope which displayed the relative abundance of a constituent as a function of atomic mass weight. After a considerable bakeout period, peaks were evident at mass numbers corresponding to carbon monoxide, carbon dioxide and the

hydrocarbons: CH_4 , C_2H_4 , C_2H_6 and C_3H_8 even when the O-ring was at room temperature. Upon cooling the valve with liquid nitrogen these peaks either disappeared or were considerably diminished in magnitude. From this analysis and with the realization that the O-ring could be a source of carbon contamination at the maximum operating temperature of the valve, an all metal valve was therefore substituted. As an additional precaution a magnetically operated baffle was installed in the vacuum channel to minimize corrosion of the copper seal in the metal valve.

With these changes the system was again run under the same conditions and a filament of 0.045 inch diameter was grown from an initial filament diameter of only 0.019 inch after only 15 minutes of operation. The unevenly deposited filament developed a hot spot and burned off before a satisfactory amount could be obtained. Chemical analyses revealed that the filament contained 211 ppm carbon. Although this was 45 percent lower than the filament obtained previously, it was still much higher in carbon than the feed material. Since contamination is more likely to occur in the initial phase of deposition on the filament, it would be expected that material of higher overall purity would be obtained had the growth of the filament continued to its maximum allowable size within the vessel. It is believed that a reduction in the carbon content could be facilitated by a bakeout of the apparatus during evacuation while the ZrI_4 capsule is in place.

SUGGESTIONS FOR FURTHER STUDY

Since the mobility of carbon in zirconium is so low as to make it essentially non-transferable in an electrotransport purification experiment, it would be very advantageous to have a small quantity of zirconium of very low carbon content (i.e. below 5 ppm) for the initial electrotransport material. These experiments attempt to show that zirconium of this quality can be obtained for a carefully designed and controlled iodide-decomposition process.

With the carbon essentially removed, electrotransport would be a very effective method of reducing the oxygen and nitrogen contents of zirconium to extremely low values. The iodide-refined zirconium could be fabricated into a rod of the dimensions required for an electrotransport purification experiment. After the steady state condition is reached the resistance ratio of the purified rod would be measured. In this way the applicability of electrotransport to the preparation of ultra pure zirconium could be evaluated.

If sufficiently high resistance ratios result from this experiment even higher purity material may be obtained by a two stage electrotransport process. The first stage would involve the purification of the iodide-refined material in a manner similar to that described in the preceding paragraph. After the high impurity concentration sections at the anode and

cathode ends are removed an additional electrotransport purification would be made.

SUMMARY

A study of the electrotransport of carbon, nitrogen and oxygen in beta zirconium was conducted. The apparatus, material and procedure necessary for obtaining the data were all described in detail. Besides the parameters of electric field strength and temperature, the data essentially consisted of a plot of the concentration profile of the specimen after electrotransport. Supporting information on the solid solubility of carbon in zirconium and the specific resistivity of zirconium at the temperatures of electrotransport was also obtained. From these data the mobility, diffusion coefficient and effective charge of carbon, nitrogen and oxygen were determined at the experimental temperatures of 1625°, 1700° and 1800°C.

This study confirmed the work of deBoer and Fast who had reported that, under the influence of a direct current, oxygen atoms move toward the anode while carbon atoms showed very little response to a direct current. The diffusion coefficients were found to be in agreement with published values.

After this information was determined an investigation into the possibility of purification by electrotransport was conducted. Using more elaborate equipment to obtain a high vacuum, electrotransport was maintained at a temperature of 1625°C until a steady state condition was reached. The

purification was evaluated by measuring the resistance ratios of sections along the length of the specimen.

The limited success of the electrotransport purification was believed to be due to the presence of carbon in the zirconium. The iodide-decomposition process was used in an attempt to obtain some material of low carbon content for further study. Many modifications of the process were required before a crystal bar of zirconium could be grown.

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